SILICON PROCESSING FOR THE VLSI ERA

VOLUME 1:

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STANLEY WOLF Ph.D.

RICHARD N. TAUBER Ph.D.

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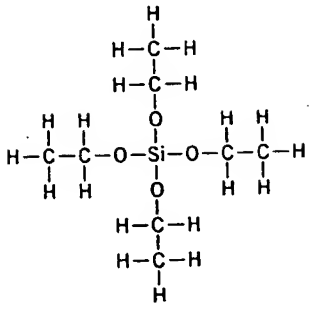
$$SiH_4\ (gas) + 2N_2O\ (gas) \xrightarrow{200\text{-}400^\circ C,\ rf} SiO_2\ (solid) + 2N_2\ (gas) + 2H_2\ (gas) \qquad (6.24)$$

Nitrogen and/or hydrogen is often incorporated in PECVD SiO_2. A low ratio of N_2O:SiH_4 will increase the index of refraction (due to the large amount of nitrogen incorporated in the film and the formation of silicon rich films). Nearly stoichiometric (n = 1.46) PECVD oxide films can be achieved by reacting SiH_4 and O_2 mixtures. The buffered HF etch rate is a sensitive measure of the film's stoichiometry and density. Lower deposition temperatures and higher N_2O/SiH_4 ratios lead to less dense films and faster etch rates. PECVD oxides also contain 2–10 at% H_2 in the form of Si-H, Si–O–H, and H–O–H, but it is less of a problem than in plasma nitride.[44] That is, the permeability of oxide readily allows outdiffusion of hydrogen on heating, whereas with impermeable nitride, destruction of the film may occur as a result of blistering when the films are heated substantially beyond their deposition temperature.[43] The hydrogen concentration is a strong function of the deposition parameters. Low deposition temperatures, high rf power, and high carrier-gas flow rates are required to prevent gas phase nucleation and its attendant particulate problems.

Plasma oxide films are generally compressive, with stress values ranging between 1×10^8–2.4×10^9 dynes/cm^2, depending on the deposition temperature and rate. Dielectric strengths of 4–8×10^6 V/cm, and dielectric constants ranging from 4–5 have been obtained. Low pinhole counts have been obtained with PECVD oxides, and adhesion to metal is also reported to be excellent.[45] However, silane-based PECVD oxides deposited with conventional capacitively-coupled rf-diode plasma sources have relatively poor step coverage and hence are seldom used. With the advent of high-density plasma sources (HDP-CVD), better step coverage and film properties are possible with silane-based chemistry. This topic is covered in Chap. 15.

6.4.1.2 Medium-Temperature LPCVD TEOS SiO_2: Use of silane as a process gas involves an inherent safety hazard. That is, silane is pyrophoric (i.e., it ignites spontaneously on contact with air). Thus, there has been an industry-wide shift away from silane chemistries. An alternate, and safer, silicon source for CVD-SiO_2 is tetraethoxysilane, $Si(OC_2H_5)_4$, also known as *TEtraEthyl OrthoSilicate*, or *TEOS*. Besides added safety, using TEOS has the benefit of providing more conformal films than those obtained from silane. This topic is discussed further in Sect. 6.4.2.

TEOS is a relatively inert material, and is a liquid at room temperature. TEOS vapor can be supplied to the reaction chamber either from a bubbler using a nitrogen carrier gas, or from a direct liquid injection system. The SiO_2 is formed by the decomposition of TEOS at elevated temperatures. The chemical structure of the TEOS molecule is shown in Fig. 6-34. Films of undoped SiO_2 from TEOS can be formed with adequate deposition rates for IC production if temperatures between 680 and 730°C are used (i.e., up to 25 nm/min). Such depositions are carried out in LPCVD tubular hot-wall batch reactors. LPCVD TEOS oxide films are used for premetal dielectrics (i.e., between the polysilicon and metal layers) and as spacers used to form lightly-doped drains (LDDs) in MOSFETs. We refer to this as a medium-temperature deposition process because the temperatures are low enough that redistribution of dopants in the substrate is not a concern, but the temperature is still too high for use over aluminum layers. As shown in Fig. 6-35a, the deposition rate drops to unacceptably small values for temperatures less than 600°C. Thus, the 675–695°C temperature range needed for practical LPCVD TEOS deposition



TEOS

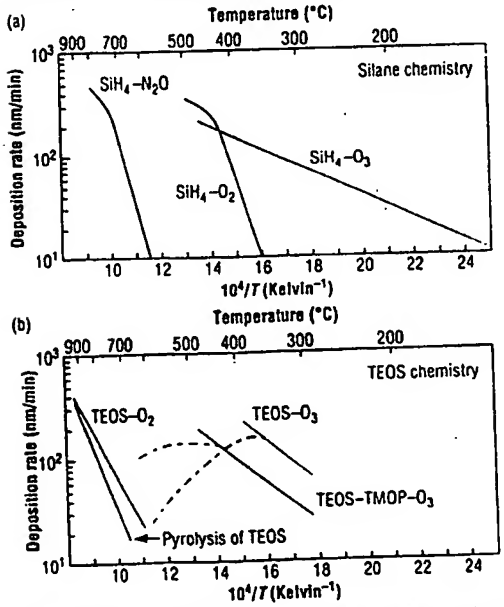
Fig. 6-34 The chemical structure of TEOS.

processes precludes their use on wafers on where Al metallization has been formed. The medium-temperature chemical reaction is:

$$Si(OC_2H_5)_4\ (liquid) \rightarrow SiO_2\ (solid) + 4C_2H_4\ (gas) + 2H_2O\ (gas) \qquad (6.25)$$

The deposition rate of TEOS SiO_2 shows an exponential increase with temperature in the range of 650–800°C (Fig. 6-35b), with an apparent activation energy of 1.9 eV.[46] This rate is also dependent on the TEOS partial pressure. It is linearly dependent at low partial pressures, and tends to level off as the adsorbed TEOS saturates the surface. LPCVD TEOS films generally show good conformality (see Fig. 6-35c).

The thermal TEOS-CVD process is carried out with highly dilute $TEOS/O_2$ feedstock mixtures. The four oxygen atoms in TEOS allow deposition of SiO_2 by pyrolysis in the absence



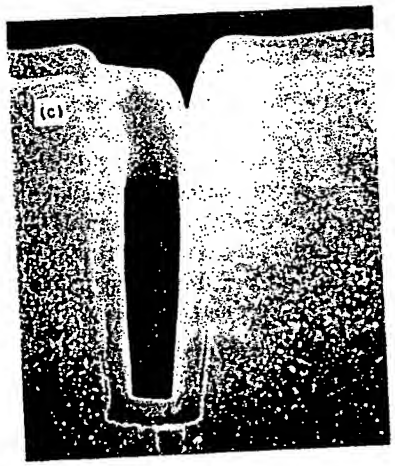


Fig. 6-35 Oxide deposition rate versus temperature for a) silane, and b) TEOS. Reprinted with permission of Solid State Technology, published by PennWell. c) Step coverage for TEOS at 640°C.

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of O_2. But highly oxygen-rich mixtures are needed for good quality films because TEOS contains carbon and hydrogen, which the O_2 burns to form CO (*gas*) and H_2O (*gas*). The O_2 also changes the intrinsic stress of the TEOS-oxide films from tensile to a low compressive stress.

Several other organosilicon compounds have been studied for LPCVD of conformal SiO_2 films at low temperatures (i.e., compatible with Al metallization). These include: diacetoxyditertiarybutoxysilane (DADBS);[47] 2,4,6,8-tetramethyltetrasiloxane (TMCTs);[48] and diethylsilane.[49]

6.4.1.3 Low-Temperature PECVD TEOS: Plasma-enhanced deposition of SiO_2 using TEOS as a source of silicon has been found to produce films at low temperatures (i.e., < 450°C) with better step coverage and gap filling characteristics than low-temperature APCVD silane-based oxides. The addition of plasma energy reduces the temperature at which adequate SiO_2 film deposition rates can be achieved. As such, this process (which made its commercial debut in the late 1980's) has found most application for forming intermetal dielectric layers in multilevel-metal technologies. PECVD-TEOS deposition is carried out at temperatures ranging from 250–425°C and at pressures of 2–10 torr, with deposition rates between 250 and 800 nm/min. An oxygen-nitrogen ambient is used with the TEOS. As is the case with thermal TEOS CVD, it was found necessary to use O_2 (with O_2:TEOS ratios ranging from 10:1 to 20:1) to minimize the inclusion of traces of C and N in the films. In the presence of a plasma, the TEOS reacts with oxygen according to:

$$Si(OC_2H_5)_4\ (liquid) + O_2\ (gas) \rightarrow SiO_2\ (solid) + \text{by-products}\ (gas) \qquad \textbf{(6.26)}$$

Hydrogen in PECVD TEOS SiO_2 films is found in concentrations ranging from 2% to 9%. The use of TEOS:O_2 for SiO_2 deposition has also been applied in a variety of PECVD reactors, such as the Concept One® and Concept Two® systems by Novellus,[50] and the Precision 5000,®[51] Centura,® and Producer® CVD systems by Applied Materials.[40] Doping of these TEOS-oxide films is done by adding trimethylborate (TMB) for boron doping, and trimethylphosphite (TMP) for phosphorus doping to the feed gases. Under optimized deposition conditions, the slope of the oxide over steps remained slightly positive (i.e., not reentrant) making void-free filling of spaces with aspect ratios of 0.8 possible.[52] However, when used as an intermetal dielectric layer on metal lines with spaces between them of 0.8 μm or less, voids are formed as the dielectric film fills these spaces. Such void formation becomes more severe as the spacing is reduced, and can reduce die yields (see Chap. 15). Void-free deposition technologies must therefore be found to overcome this problem, and it is the next issue discussed.

6.4.1.4 Ozone TEOS: Under APCVD, the addition of O_2 to TEOS does not sufficiently raise the deposition rate at temperatures below 500°C to make the process economically feasible for IC production.[53,54] However, by adding ozone (O_3) to the TEOS vapor it is possible to obtain deposition rates using APCVD which are comparable to those of SiH_4/O_2 at 400°C (and without the need for employing a plasma). For example, at 300°C deposition rates of 100–200 nm/min have been obtained with 4% O_3, while at 400°C this rate occurs with 1–2% O_3. Ozone produced from oxygen can be present at concentrations of up to 10% O_3 in O_2. An in-line *ozonator* is used to produce the ozone (see Fig. 6-36). The mechanisms of deposition of SiO_2 from TEOS and O_3 are described in Ref. 75. The films from TEOS/O_3 can be deposited as undoped silicate glass USG (used for intermetal dielectrics) or as BPSG (used for pre-metal dielectrics, with such gases as TMB and triethylorthophosphate TEOP employed as the dopant sources). The SiO_2 films produced from TEOS/O_3 exhibit high conformality and outstanding ability to fill shallow